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The structure of prospective denox catalysts based on carbon–montmorillonite nanocomposites

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Abstract

Montmorillonites modified with carbon deposits were reported to be promising catalysts of NO reduction with ammonia (SCR). The influence of different preparation methods on structural, textural and sorption properties were discussed. Three preparation methods were considered, differing in the pretreatment of the clay preceding the introduction of carbon precursor (polymer soluble in water). The structure was studied by XRD, texture by sorption of argon, benzene and carbon tetrachloride and surface composition by XPS. The obtained nanocomposites had different textural properties, depending on pretreatment. XPS, TPD and textural data suggest different mechanisms of formation of nanocomposites on untreated and acidic pretreated clays. The introduction of carbon deposits influenced hydrophilic properties. The number of ammonia sites changed after each preparative step: acidic pretreatment, pillaring and the formation of carbon deposits.

Keywords: Montmorillonite; Carbon deposits; Texture; Sorption; NH_3; H_2O

1. Introduction

Catalytic reactions are the most efficient methods of pollution abatement. Selective catalytic reduction of NO with ammonia on vanadia–titania catalyst is a widely applied industrial method [1]. It suffers, however, from some disadvantages—among others, its application range concerns medium temperatures (from ca. 250 to ca. 400 °C). It would be of advantage to develop a new catalyst, active and selective at low temperature, specially around 150 °C, the typical temperature of outlet stack gases (after precipitator and desulfurization unit). Carbonaceous materials were found to be promising in this matter [2–8] but on one hand, when cheap active carbons are used, they are difficult to prepare in the monolith form, and on the other hand, present prices of carbon fibers which may be formed into monoliths, are rather high. A possible solution are carbon–inorganic nanocomposites which would show some properties of both types of materials. One of inorganic candidates are montmorillonites—layered clays with the possibility of extensive modification of their textural and surface properties. Chmielarz et al. [9] showed that promoting both untreated or pretreated (with acid or pillared) montmorillonites with carbon deposits increased NO reduction with ammonia (cp. Fig. 1).

Additionally, there is a possibility of the use of waste montmorillonite sorbents (deactivated e.g. in vegetable oil industry) as supports, as shown by Grzybek et al. [10,11] which after carbonization also show carbon deposits on the surface. The preparation of montmorillonites covered with carbon deposits may be realized by different routes, as proposed in literature: pyrolysis of organic substances previously introduced into the structure of clay [12–14], adsorption of polymers [15–29] or direct synthesis of the clay precursor in the presence of an organic substance [30]. In most cases, however, the preparation was used not in order to change the properties of the inorganic substance but to obtain (after proper extraction) carbonaceous materials with special properties.

However, little is known about the influence of preparative steps on the structure of such materials as described by Chmielarz et al. [9]. The subject of the present work was a detailed analysis of each step of preparation (simi-

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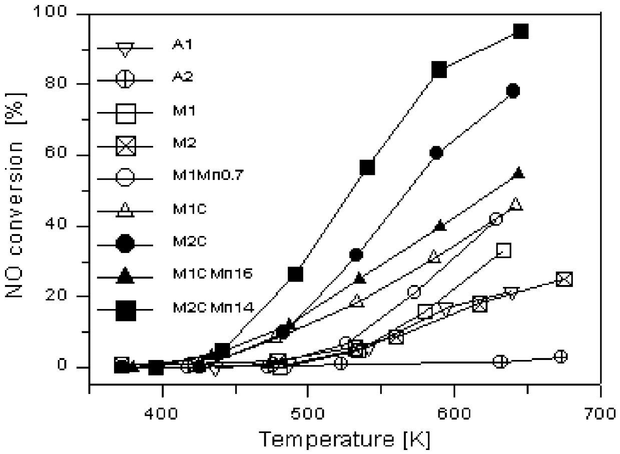


Fig. 1. NO conversion for carbon modified differently pretreated montmorillonites. Designation of the samples—A: unpillared clay (1, untreated; 2, activated with HCl); M: pillared clay (1, based on A1; 2, based on A2); MxC: modified with carbon deposits; MxCMn: promoted with MnO_x ([9] by permission of the editor).

lar to that leading to carbon–montmorillonite nanocomposites shown in Fig. 1) and their influence on the structure of the obtained materials and their sorption properties towards ammonia. The routes used in this work included different pretreatments of clay and the introduction of the precursor of carbon deposits by polymer sorption at different stages of the preparation: (a) the polymer was introduced by sorption on the untreated clay, or (b) clays were pillared with aluminum hydroxycations and the polymer was then introduced by sorption, or (c) the clay underwent acidic pretreatment, was then pillared and the polymer was adsorbed. In each case, the last preparative step was carbonization in nitrogen in order to obtain stable carbon deposits. The polymer used was a commercial polyacrylamide soluble in water [31–34].

2. Experimental

2.1. Detailed preparation of the studied samples [31–34]

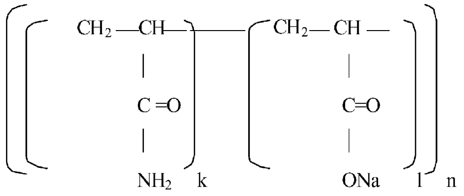
The starting material was montmorillonite obtained by sedimentation from bentonite from Milowice (Poland). Three preparative routes were used: A, B or C.

Route A included the sorption of polymer directly on the sodium form of montmorillonite. Aqueous suspension of montmorillonite and aqueous solutions of commercial polymer (polyacrylamide) were contacted for 48 h at room temperature under constant stirring. The concentration of polymer was 2, 5 or 10 wt.%. After sorption, water was removed by evaporation and the pelleted montmorillonite was carbonized in nitrogen at 623 or 773 K for 30 min [31].

In route B, the first step was pillaring with chlorhydrol according to the method of Vaughan and Lussier [35]. Then the polymer was sorbed from aqueous 0.1, 0.2, 0.5, 1, 2, 3, 5 or 10 wt.% solutions for 24 h. Dried and pelleted samples were carbonized at 673 or 773 K in nitrogen for 30 min [32,33].

Route C started with the acidic pretreatment of the sodium form of montmorillonite, which was carried out by 20% HCl for 30, 60 or 90 min—the ratio of montmorillonite to HCl was 5 g to 100 ml of 20% HCl solution. Then pillaring with Al hydroxycations was carried out using chlorhydrol, followed by polymer sorption from 3% solution for 24 h and carbonization in nitrogen for 30 min at 773 K [34].

The polymer used as precursor of carbonaceous deposits was in all cases polyacrylamide (commercial name Gigtar):



$$\left[\left(\begin{array}{c}\mathrm{CH_2-CH}\\ |\\ \mathrm{C=O}\\ |\\ \mathrm{NH_2}\end{array}\right)_k-\left(\begin{array}{c}\mathrm{CH_2-CH}-\\ |\\ \mathrm{C=O}\\ |\\ \mathrm{ONa}\end{array}\right)_l\right]_n$$

Designation of the samples comprises: the type of preparation method (A, B or C), pretreatment time (30, 60 or 90), pillaring (Al) and the addition of carbon deposit (C). An additional number at the end of the designation of the sample denotes the concentration of polymer solution used but for the sake of clarity it is given only in case when it was different from 3%. Thus e.g. sample C30Al was prepared by acidic pretreatment of montmorillonite for 30 min and then pillared with Al with no sorption of polymer, while C30AlC designates montmorillonite which, additionally to the above mentioned treatments, underwent sorption of polymer from 3% solution and carbonization and thus contained carbon deposits; and for sample BAlC0.1, preparation consisted of pillaring untreated montmorillonite, sorption of polymer from 0.1% solution and carbonization. Table 1 comprises the preparative details for all samples described in this work.

2.2. Characterization methods

The following methods of characterization were used:

- Structure by X-ray diffraction XRD using Philips PV 3020 X'Pert and Cu Kα radiation (line $\lambda = 0.15418$ nm).
- Texture by sorption of argon at 98 K and benzene or carbon tetrachloride at 295 K.
- Surface composition by X-ray photoelectron spectroscopy (XPS). The spectra were recorded with a Leybold AG spectrometer equipped with a Mg Kα source and a multichannel plate analyzer working in FAT mode ($\Delta E =$ const.) at a pass energy of 29.6 eV. The samples were studied in the form of pellets loosely packed onto the sample holder. The pressure in the main chamber was better than 3×10^{-8} mbar. The spectra were smoothed, a non-linear background was subtracted and the fitting was carried out with a 50/50 Lorentz and Gauss curves. Si 2p at a binding energy of 103.1 eV (typical for montmorillonites) was used as a calibration standard. The composition of the

Table 1
The preparative details and the designation of the samples

Sample	Pretreatment		Pillaring	Polymer sorption/concentration of polymer (wt.%)	Carbonization or calcination temperature (K)
	Type	Time (min)			
M	–	–	−	−	–
AC5	–	–	−	+/5	773
AC5	–	–	−	+/5	623
AC10	–	–	−	+/10	773
AC10	–	–	−	+/10	623
BAl	–	–	−	−	773
BAlC0.1	–	–	+	+/0.1	773
BAlC0.5	–	–	+	+/0.5	773
BAlC	–	–	+	+/3	773
C30	HCl	30	−	−	773
C30Al	HCl	30	+	−	773
C30AlC	HCl	30	+	+/3	773
C60	HCl	60	−	−	773
C60Al	HCl	60	+	−	773
C60AlC	HCl	60	+	+/3	773
C90	HCl	90	−	−	773
C90Al	HCl	90	+	−	773
C90AlC	HCl	90	+	+/3	773

samples was calculated using the areas of the appropriate peaks and the sensitivity factors of Wagner et al. [36].

- Hydrophilic properties by water vapor sorption at 298 K using a standard volumetric equipment.
- Ammonia sorption (physical and chemical) at 273 K using the following method: measurement of isotherm I at 273 K, followed by evacuation at the same temperature and subsequently isotherm II again at 273 K. Thus isotherm I represents a sum of physical and chemical adsorption, isotherm II is connected only with physical adsorption, and the difference between isotherms I and II is the chemisorbed amount.

3. Results and discussion

3.1. Structure

3.1.1. The influence of different preparative steps

The influence of the following preparative steps on the structure of montmorillonites covered with carbon deposits was considered [31–34]:

- acidic pretreatment of montmorillonites,
- pillaring with Al hydroxycations,
- introduction of polymer between clay layers either previously pillared or without pillaring,
- carbonization at different temperatures or using different modes.

Fig. 2 shows as an example, $d_{0\,0\,1}$ values and S_{BET} for unpillared montmorillonites before and after sorption of polymer and carbonization at 623 or 773 K. As it may be seen from the figure, after polymer sorption and carbonization at lower temperature, $d_{0\,0\,1}$ increased but the surface area decreased in comparison to the non-modified sample M (from 41.7 for M to under 10 m^2/g for AC10 and ca. 20 m^2/g for AC5). The increase in $d_{0\,0\,1}$ depended on the concentration of polymer solution—the higher the concentration, the higher $d_{0\,0\,1}$. The application of higher carbonization temperature decreased $d_{0\,0\,1}$ practically to that of M and increased S_{BET} to an extent depending on polymer concentration (cp. Fig. 2a and other

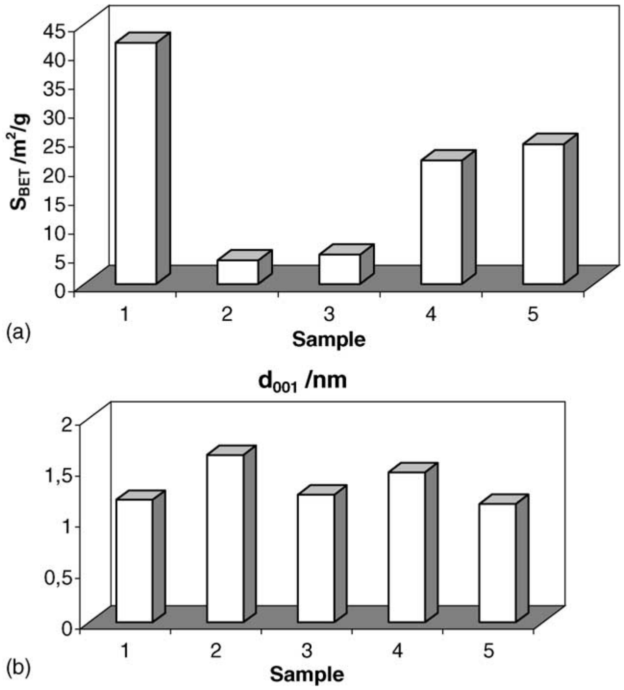


Fig. 2. Specific surface area S_{BET} (a) and $d_{0\,0\,1}$ (b) for montmorillonite after polymer sorption and carbonization at 623 or 773 K. Samples: 1, M; 2, AC10 carbonized at 623 K; 3, AC10 carbonized at 773 K; 4, AC5 carbonized at 623 K; 5, AC5 carbonized at 773 K.

data not depicted [31]). This suggests that the polymer is sorbed between clay layers thus increasing d_{001} spacing and during carbonization it is partly or totally gasified and does not form a porous layer. Sorption of polymer on the internal layers of clay minerals was also found by other authors, e.g. Levy and Miller [37] or Asselman and Garnier [38].

Acidic pretreatment of montmorillonites did not influence d_{001}, thus testifying the presence of some undisturbed layers. However, simultaneously the specific surface area increased considerably from 41 m^2/g for non-modified sample to 156, 210, or 209 m^2/g for C30, C60 and C90, respectively. This suggests that some clay layers were destroyed by the acidic pretreatment that removed Al, and SiO_2 formed "pseudo-pillars". Since this was not detected separately in XRD, it may be assumed that this "pillared" part was delaminated. The partial destruction of the clay structure was proven by the change in the Al/Si ratios determined by XPS: 0.314, 0.252 and 0.186 for C30, C60 and C90, respectively [34].

Pillaring with Al hydroxycations led to an increase in d_{001} from 1.2 nm for M to 1.8–1.9 nm for all pillared samples, both on pretreated and untreated M. Sorption of polymer and the following carbonization did not influence this parameter.

Table 2 summarizes specific surface areas S_{BET} for selected samples obtained by method B or C in comparison to calcined montmorillonite (M) [33,34].

From Table 2 and other data, it may be derived that S_{BET} increased after pillaring, to an extent depending on the starting structure of clay—a higher relative increase was registered for untreated clay than that pretreated with acid: cp. M versus BAl (41.7 and 405 m^2/g), C30 versus C30Al, C60 versus C60Al, C90 versus C90Al (156 and 291; 210 and 326; 209 and 367 m^2/g, respectively).

After the sorption of polymer S_{BET} decreased again depending on: (i) the concentration of polymer solution—the higher the concentration, the lower the resulting S_{BET}; (ii) the type of pretreatment—when samples from B and C series are compared for the same concentration of polymer solution, it may be seen that S_{BET} is lower, when no pretreatment or short pretreatment was used (resulting samples BAlC and C30AlC, respectively), then it increased for medium pretreatment time (C60AlC) and again decreased for the sample based on montmorillonite which underwent the longest acidic pretreatment (C90AlC). It must be additionally added that the elemental composition differed after polymer sorption and carbonization for B and C series: the carbon content was near to 1% for all samples obtained from 3% solution (1.0; 0.9; 1.3 and 1.3 wt.% for BAlC, C30AlC, C60AlC and C90AlC, respectively), but the nitrogen content was 1.1 wt.% for BAlC and only 0.1 wt.% for C90AlC. The changes in S_{BET} and in texture, described below, as well as elemental composition suggest that there is a different structure and/or distribution of the carbon deposits caused by differences in the mechanism of its formation on the surface. This is additionally proven by TPD studies by Grzybek et al. [34] which showed a different profile of $m/e = 44$ (CO_2) for C30-, C60- and C90-based samples. A possible explanation of the above observations may be connected with the acidity of clays, which were used as the first cracking catalysts. It is speculated by Grzybek et al. [34] that for more acidic samples (those pretreated with HCl, especially for longer periods) cracking of adsorbed polymer either preceded carbonization or competed with it, resulting in smaller carbon deposits.

Table 2
Specific surface area S_{BET} for selected samples obtained by method B or C [33,34]

Sample	S_{BET} (m^2/g)
M	41.7
BAl	405
BAlC0.5	317
BAlC	92
BAlC5	54
C30	156
C30Al	291
C30AlC	82
C60AlC	211
C90AlC	111

3.2. Texture

Textural properties were studied by sorption of molecules of different size: Ar, C_6H_6 and CCl_4. The method of Brunauer and Mikhail based on the "t" curve showed that the introduction of polymer to non-modified pillared clay led to the decrease in both radius of smaller pores and the volume of bigger pores [33]. It was assumed to be caused by the deposition of a layer or islands of carbon in bigger pores, thus leading to their narrowing. The decrease in micropore volume was interpreted as the exclusion of some pores by blocking them or their inlets through the formation of the mentioned deposits [33]. Fig. 3 depicts the micropore distribution for C series.

From Fig. 3, it may be seen that the character of changes in micropores is a complicated function of the time of acidic activation. The micropore volume for the samples shown in Fig. 3 forms a sequence: C30AlC < C90AlC < C60AlC. Thus a simple trend does not exist. Sample C30AlC seems to be more similar to BAlC described in [33] than to the others pretreated with acid. Possibly these complicated changes have their origin in different acidity of the starting montmorillonites, which differs as will be described below. If this is so, the following hypothesis may be given: for non-modified or weakly acidic starting clays (B and C30) carbon deposits are bigger and penetrate the porous system to a smaller extent while with the increase in acidity deposits become smaller and may penetrate the system more deeply. Such an effect may be observed in XPS which gives information on the first 2–20 monolayers from the outer surface of the grain and is therefore sensitive to the distribution within the catalyst particle. If the distribution is uneven and more polymer

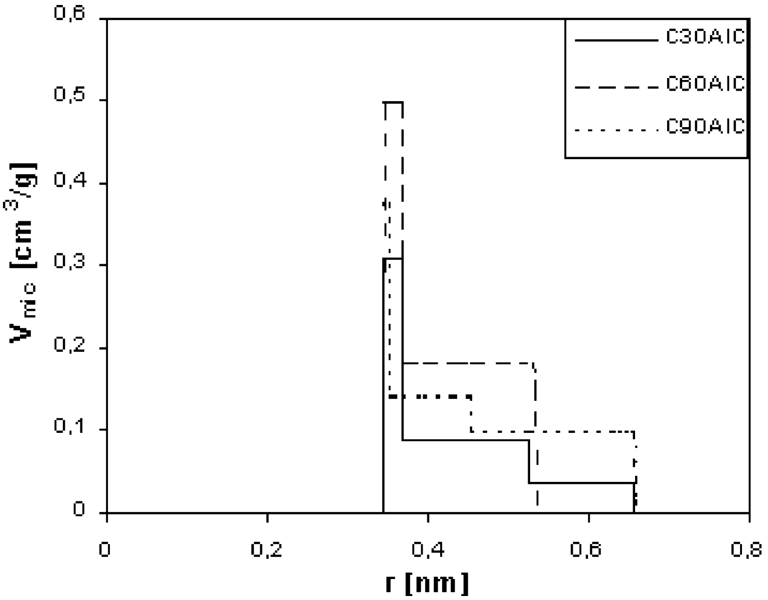


Fig. 3. The distribution of micropores for carbon modified montmorillonites obtained in series C.

is deposited on the outer surface of clay particles than inside the pores, intensity ratio of the modifier (carbon) to support (Si or Al) should be higher than in case of more even distribution. XPS data of Grzybek et al. [32] showed that the amount of carbon registered in XPS was a linear function of the Si and Al content for B series. Table 3 compares XPS intensity ratios for C/Si and C/Al for nanocomposites from series C and B prepared using the same polymer concentration.

As XPS gives information about the concentration of elements on the outer surface and in the first 2–20 monolayers of clay particles, the decrease of C/Si and C/Al with the time of acidic activation seems to confirm that more carbon enters the porous system for montmorillonites activated with HCl for longer periods. Simultaneously, it must be mentioned that the specific surface area decreased rapidly upon carbon modification (e.g. from 367 to 111 m^2/g for C90Al and C90AlC, respectively) but, taking into account that the studied systems were microporous, that still means that introduced deposits must be of nanometer—or sub-nanometer—size or otherwise they would block the porous system completely.

Fig. 4 compares specific surfaces area S_{BET} obtained from sorption of Ar, C_6H_6 and CCl_4. The kinetic diameter for argon is ca. 0.33 nm while it is ca. 70% higher for C_6H_6 and CCl_4 [39]. Because clays are microporous, the accessibility of the systems is reflected by different amounts of sorbed molecules of varying sizes.

From Fig. 4 it may be seen that for most samples, the values of specific surface area calculated from sorption of benzene and carbon tetrachloride were smaller than those obtained from Ar. This indicates the presence of small pores not penetrated by the first two molecules but accessible to Ar. Fig. 4 shows some additional tendencies to those derived from the values of S_{BET} (Ar) described above: (i) values of specific surface area for clays modified with acid (C30, C60 and C90) were similar for Ar, C_6H_6 and CCl_4 while they were quite different for pillared samples (BAl, C30Al, C60Al, C90Al), indicating that the clays pretreated with acid had most micropores accessible to the same extent by all

Table 3
XPS intensity ratios for nanocomposites from C series in comparison to B

XPS ratio (at.%/at.%)	Sample			
	C30AlC	C60AlC	C90AlC	BAlC
Al/Si	0.613	0.565	0.53	0.67
C/Si	0.671	0.443	0.414	1.05
C/Al	1.093	0.785	0.832	1.44
Elemental content of C (wt.%)	0.9	1.3	1.3	1.0

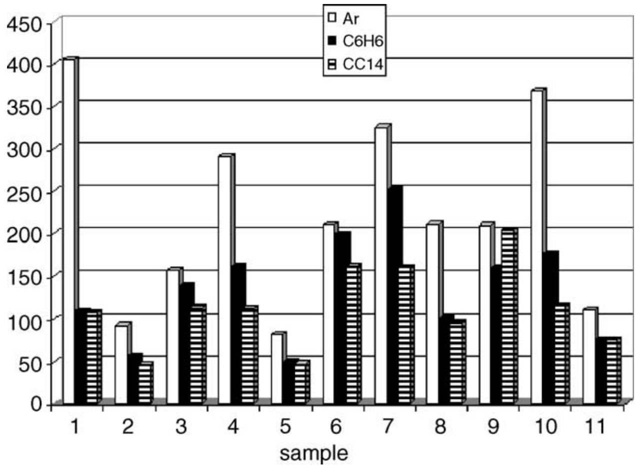


Fig. 4. Specific surface area for the studied samples. Samples: 1, BAl; 2, BAlC; 3, C30; 4, C30Al; 5, C30AlC; 6, C60; 7, C60Al; 8, C60 AlC; 9, C90; 10, C90Al; 11, C90AlC (cross-sectional area (nm^2/molecule): 0.162, 0.46 and 0.64 for Ar, C_6H_6 and CCl_4, respectively).

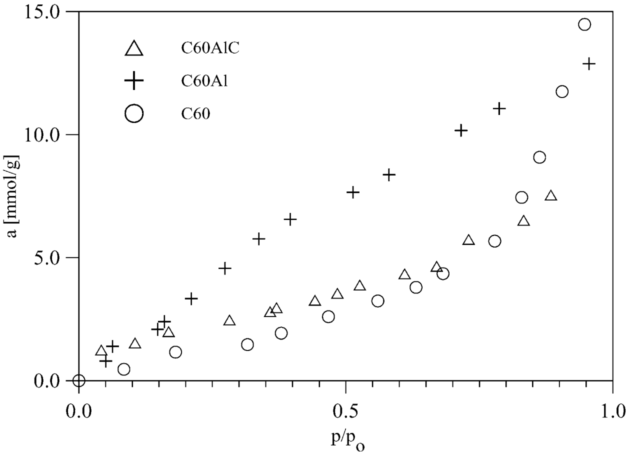


Fig. 5. Water vapor isotherms at 298 K for samples of C series.

three molecules while pillaring introduced a considerable amount of smaller micropores; (ii) the introduction of carbon deposits led to a higher decrease in S_{BET} (Ar) than S_{BET} (C_6H_6 or CCl_4) which suggests that carbon was deposited either inside the small micropores and/or at their inlets, thus rendering them inaccessible to Ar.

3.3. Hydrophilic properties

Water vapor sorption isotherms are shown as an example for C60, C60Al and C60AlC in Figs. 5–7 compare the amounts of adsorbed water versus relative pressure for pillared clays based on untreated montmorillonite (BAl) or clays pretreated with HCl (C30Al, C60Al and C90Al) and clays pillared and modified with carbon (BAlC, C30AlC, C60AlC and C90AlC), respectively.

From Figs. 5–7 it may be derived that the introduction of carbon deposits influenced the hydrophilic properties of the systems. There is a change of the shape of isotherms from BET type III (pretreated montmorillonites, e.g. C60) to type II (clays pillared e.g. C60Al or pillared and modified with carbon deposits e.g. C60AlC). Similar results were registered for the C60 and C90 series. Pillaring led to an increase in H_2O sorption. In the relative pressure range up to 0.45, the amount sorbed for pillared clays practically did not depend on the initial acidic pretreatment. In the higher pressure range, the amounts of H_2O adsorbed for BAl and C30Al are ca. 1/3 smaller than for C60Al and C90Al (cp. Fig. 6). The introduction of carbon deposits decreased the hydrophilic properties calculated per gram in the following sequence: C30AlC > BAlC > C60AlC ≈ C90AlC (cp. Fig. 7). It should be taken into account, however, that the considered systems vary widely with respect to specific surface area and microporosity. Fig. 8 shows the amounts of water sorbed on 1 m^2 of the samples. They form a sequence: C30AlC > BAlC > C90AlC > C60AlC which means that the number of hydrophilic sites per surface area unit is the highest for C30AlC and the smallest for C60AlC. The results may be understood if one takes into account that H_2O molecules are smaller than Ar atoms (kinetic diameter 0.27 nm versus 0.33 nm [39]) and they may thus

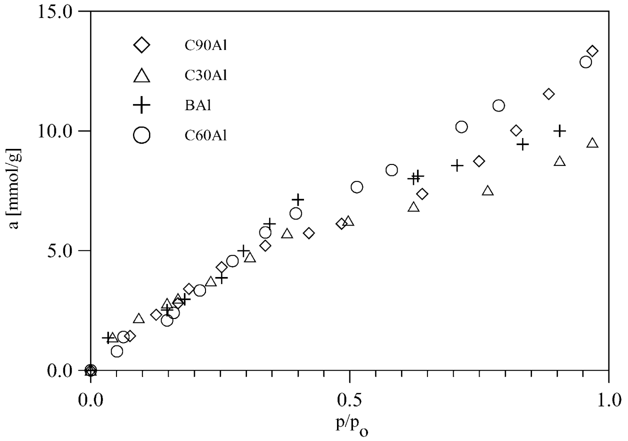


Fig. 6. The comparison of the amounts of adsorbed H_2O (mmol/g) as a function of relative pressure for pillared samples.

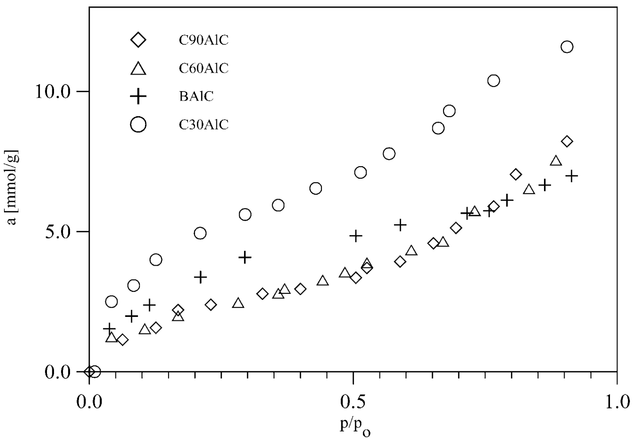


Fig. 7. The comparison of the amounts of adsorbed H_2O (mmol/g) as a function of relative pressure for samples pillared and modified with carbon.

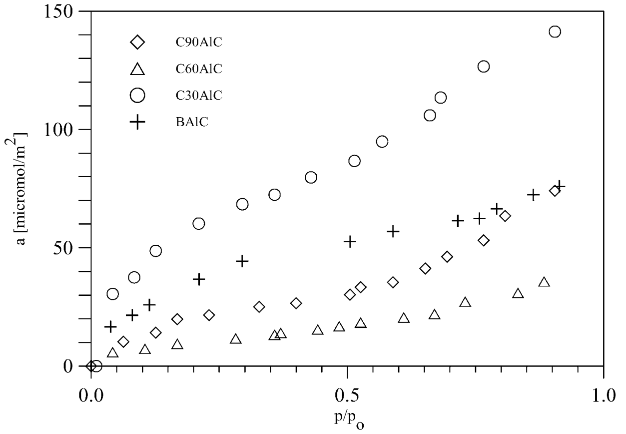


Fig. 8. The amounts of water adsorbed per 1 m^2 (μmol/m^2) as a function of relative pressure for samples pillared and modified with carbon.

Table 4
The amount of chemisorbed ammonia a_{chem} for differently prepared carbon–montmorillonite composites

	Sample										
	BAl	BAlC	C30	C30Al	C30AlC	C60	C60Al	C60AlC	C90	C90Al	C90AlC
a_{chem} (mmol/g)	1.0	0.5	0	0.7	0.42	0	0.9	0.3	0.3	0.6	0.44
a_{chem} (μmol/m^2)	2.6	5.1	0	2.4	5.12	0	2.7	1.4	1.4	1.7	3.97

penetrate micropores inaccessible to Ar. The data depicted in Fig. 8 are obtained by dividing the sorbed amount of H_2O by specific surface area calculated from Ar sorption data. Therefore, as the presence of micropores inaccessible to Ar leads to the underestimation of specific surface area, one obtains higher number of H_2O molecules sorbed per 1 m^2. In connection with the previous discussion concerning the penetration of the porous system with carbon deposits, it seems that in the case of C30AlC with the smallest S_{BET} carbon deposits rather narrow the smallest micropores than cut them of completely. Using the same reasoning for C60AlC would lead to a conclusion that the porous system is not so narrow in this case and Ar atoms can penetrate it to a greater extent than in the case of C30AlC. This is in good agreement with the conclusion that carbon deposits formed smaller units inside the porous system as suggested by XPS for C60AlC in comparison to bigger deposits on the outer surface for C30AlC. Thus sorption of H_2O reflects both changes in porosity and the number of hydrophilic sites.

3.4. Ammonia sorption

Fig. 9 shows as example isotherms I and II of ammonia for C90Al. From the difference of isotherms I and II the chemisorbed amount of ammonia was calculated, as given in Table 4.

The analysis of Table 4 suggests that: (i) The acidic activation of clay for 30 and 60 min does not lead to the formation of considerable amount of acidic sites, but a 90 min pretreatment does so. (ii) Pillaring increased the total number of acidic sites (cp. C30 versus C30Al; C60 versus C60Al or C90 versus C90Al). This is in good agreement with literature. Taking into account the investigations of Chae et al. [40] it may be assumed that they are of Lewis type. The comparison of pillared samples with different initial pretreatments forms a sequence (mmol/g): C90Al < C30Al < C60Al < BAl. This indicates that there is no simple correlation between the time of modification (or its lack) and the total number of sites. It is possible that this complicated pattern observed is connected with different density of pillars for the studied systems, as suggested by Chae et al. [40]. However, this problem needs some more experimental data. (iii) The introduction of carbon deposits decreased the amount chemisorbed per gram but acidity calculated per square meter increased (with the exception of high-area sample C60AlC). As the NH_3 molecule has a very similar kinetic diameter as H_2O, the molecular sieve effect seems to play the most important role. This would mean that some NH_3 necessary for SCR reaction is stored in the smallest pores. These smallest pores are inaccessible to bigger molecules e.g. sulfur dioxide (kinetic diameter slightly higher than Ar [39]) and this perhaps would explain why catalysts based on pillared clays modified with carbon deposits were only slightly poisoned by SO_2 molecules present in an SCR reaction mixture, as observed by Chmielarz et al. [41].

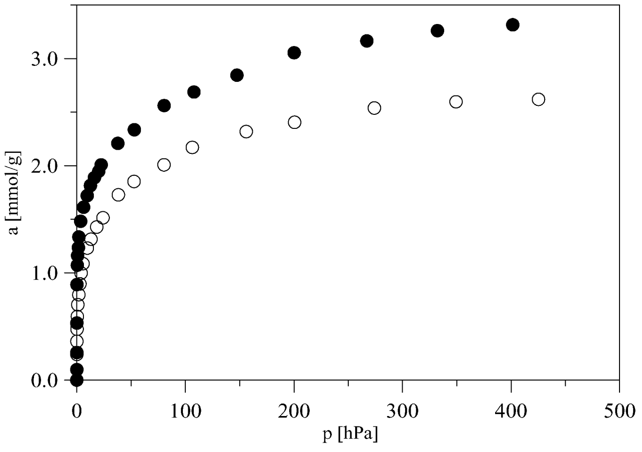


Fig. 9. Ammonia sorption (mmol/g) at 298 K for C90Al. (●) Isotherm I: physical and chemical sorption; (○) isotherm II: physical sorption.

4. Conclusions

Montmorillonites modified with carbon deposits were shown previously to be promising SCR catalysts. However, they may be obtained by different preparation routes. Structural, textural and sorption properties of such systems depend strongly on the procedure used and may thus influence SCR performance.

Sorption studies proved that the pillared montmorillonites had considerable specific surface areas. XRD results showed that the samples were stable and it was possible to introduce carbon deposits onto their inner surface without change in the structure. For unpillared clays, polymers were introduced between clay layers, but the solids resulting from carbonization were practically non-porous.

The obtained nanocomposites had different textural properties, as may be derived from the analysis of specific surface area obtained by sorption of molecules of different size (Ar, C_6H_6, CCl_4).

XPS, TPD and textural data pointed to different distribution of carbon deposits for differently pretreated montmorillonites (either acid pretreated or untreated). This suggests different mechanisms of formation of nanocomposites in these cases.

The introduction of carbon deposits influenced the hydrophilic properties of the systems.

The number of ammonia sites changed after each preparative step: acidic pretreatment, pillaring and the formation of carbon deposits.

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